

Chapter 2

EXPLANATION OF THE COLOSSAL DETONATION SENSITIVITY OF SILICON PENTAERYTHRITOL TETRANITRATE EXPLOSIVE

Overview

For applications requiring high shattering power, it is desirable to increase detonation velocity so the energy can be released faster to achieve higher power output. One way to achieve this goal is to increase the density of energetic material. Based on this idea, a new silicon-based explosive was recently synthesized by the nitration of tetrakis(hydroxymethyl)-silane, $\text{Si}(\text{CH}_2\text{OH})_4$, with nitric acid¹. This sila-pentaerythritol tetranitrate (Si-PETN), $\text{Si}(\text{CH}_2\text{ONO}_2)_4$ (tetrakis(nitratomethyl)-silane) has a molecular structure nearly identical to its carbon analog - pentaerythritol tetranitrate (PETN), $\text{C}(\text{CH}_2\text{ONO}_2)_4$ - with the central carbon atom replaced by silicon, resulting in higher density than the original PETN. Unexpectedly, Si-PETN shows dramatically increased sensitivity, exploding with just a touch of a spatula (no impact), more sensitive than mercury fulminate and far more sensitive than PETN, making it extremely dangerous and difficult to study. Detonation sensitivity is an extremely important issue in explosives, involving many factors, such as the crystal orientation and morphology^{2,3}, hot spot formation⁴⁻⁶, bandgap⁷, and the distribution of electrostatic potential^{8,9}. However, there is no clear understanding about the molecular and structural determinants controlling their sensitivity to external stimuli. Since the molecular structures of PETN and Si-PETN are very similar with very similar contacts between various molecules in the crystal, we considered that elucidating how replacing the central C with Si dramatically increases sensitivity might provide clues useful for understanding sensitivity in other systems. In this chapter I carried out DFT calculations on pathways for unimolecular decomposition and showed that there exists a unique pathway that differentiates PETN and Si-PETN, which suggests an explanation of the colossal sensitivity.

Computational methods

All calculations were carried out with Jaguar 7.0 package¹⁰, using the unrestricted hybrid functional UB3LYP¹¹ and UM06¹² to locate all the stationary points and to calculate Hessian matrix for zero point energy and reaction enthalpy at 6-311G** level. Data in the Table 2.1 for small nitrate esters show that B3LYP tends to underestimate the O-N Bond Dissociation Energy (BDE) by ~ 5 kcal/mol, in agreement with previous calculations¹³, while the M06 functional generally reproduces the experimental BDEs¹⁴. Thus M06 leads to a BDE for reaction 1 (see Figure 2.1) in PETN of 39.0 kcal/mol, within the range of experimental values of 35.0¹⁵, 39.5¹⁶ and 45.9¹⁷ kcal/mol. Consequently we will quote only the M06 values below.

Table 2.1 Comparison of B3LYP and M06 for various bond energies (in kcal/mol). We conclude that the M06 is more accurate.

O-N BDE	B3LYP	M06	Experiment ⁶
Methyl-nitrate	35.5	42.5	41.2±1.0
Ethyl-nitrate	34.1	42.1	41.0±1.0
propyl-nitrate	36.2	44.3	42.3±1.0
Iso-propyl-nitrate	36.0	44.2	41.1±1.0
C-O BDE	B3LYP	M06	Experiment
Methyl-nitrate	75.0	83.6	81.0±1.0

Results and discussion

Five different reaction pathways were studied, as shown in the Figure 2-1. NO₂ dissociation (reaction 1) generally provides the lowest barrier for unimolecular decomposition of energetic materials with nitro group, such as RDX¹⁸, PETN¹⁵⁻⁹, and HMX¹⁹ although HONO elimination (reaction 3) is

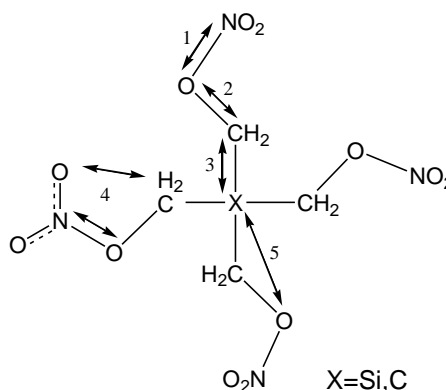


Figure 2-1. The structure of PETN (X=C) and SiPETN (X=Si) and five reactions studied in this work.

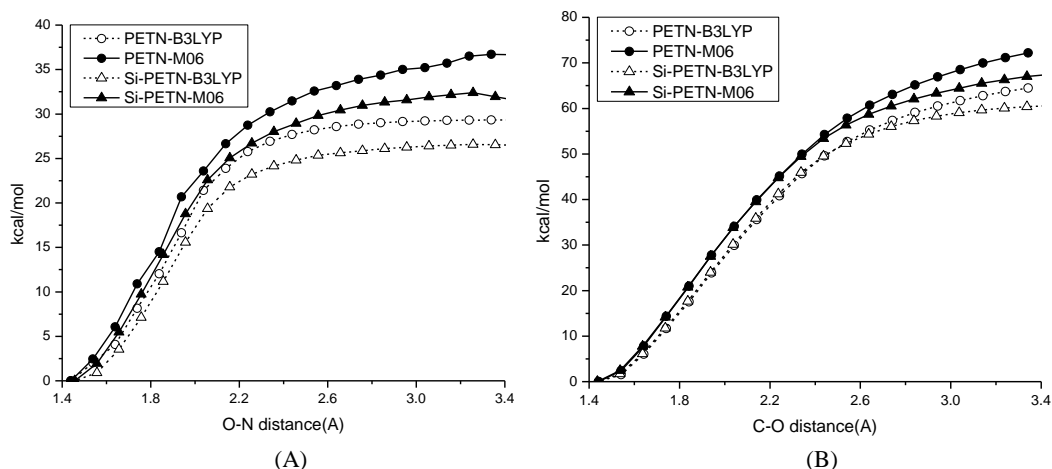


Figure 2-2 (A) O-N bond (B) C-O bond scan by B3LYP and M06 at 6311G** level. Zero point energies are included.

often close. The calculated O-NO₂ BDEs are 39.0 kcal/mol for PETN and 35.6 kcal/mol for Si-PETN. The O-N bond scans are shown in Figure 2-2A. This lower O-N bond energy of Si-PETN may facilitate the propagation of chain reactions to contribute partially to its sensitivity. However, this reaction is not exothermic and it is *not* the decomposition pathway with the lowest barrier, as discussed below.

The C-O bond-breaking (reaction 2) leads to BDE = 82.2 (C) and 77.6 (Si), as shown in Figure 2-2B. With such high barriers, they would only be observed in high energy laser experiments²⁰ and would not explain the difference in sensitivity.

The potential energy surface near the transition state to break the X-C bond (reaction 3) is very flat (see Figure 2-3), making it difficult to locate the precise transition state. Consequently, we carried out a 2-D scan of the X-C and O-NO₂ bond lengths, which shows that the central Si-C bond of Si-PETN and C-C bond of PETN are strongly dependent on the O-NO₂ bond. Stretching the O-NO₂ bond weakens the X-C bond because the oxygen forms a C=O double bond by withdrawing electron density from the X-C bond. The product of this reaction is CH₂O, NO₂, and a tertiary C/Si free radical. The lower electronegativity of Si (1.8) compared to C (2.5), explains the drastically different charges on the central atoms: -0.19 in PETN +0.25 in Si-PETN (B3LYP, with similar

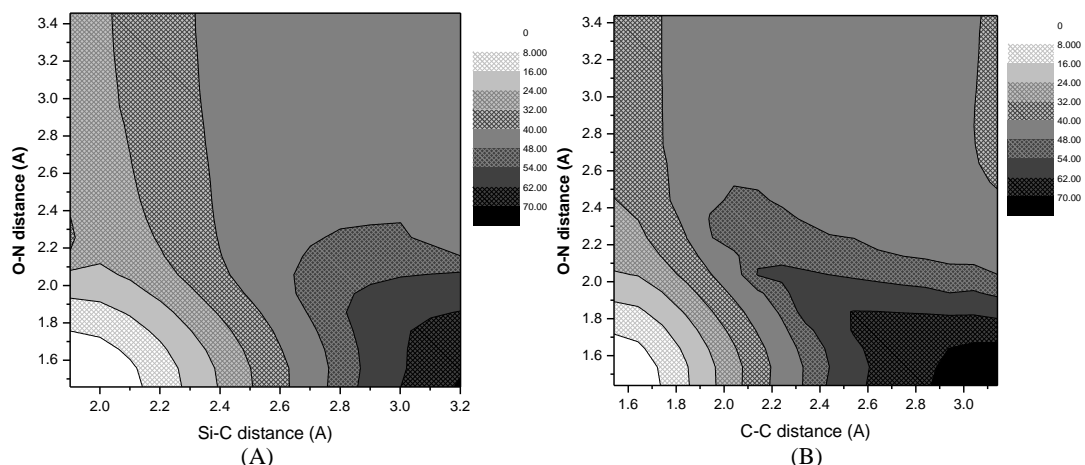


Figure 2-3 Two dimensional scans of (A) Si-C and O-N bond of Si-PETN (B) C-C and O-N bond of PETN by B3LYP at 6311G** level.

trends from M06). However the similar transition state (TS) barriers of 51.3 kcal/mol (C) and 49.7 kcal/mol (Si) would not explain the difference in sensitivity.

Next we examined HONO dissociation (reaction 4) involving simultaneous formation of a new OH bond with breaking of the O-NO₂ bond, as shown in Figure 2-4. This is a well known mechanism for energetic molecules with the nitro group, discovered first in DFT calculations¹⁸, which leads to an activation energy of 39.2 kcal/mol for RDX¹⁸ and 44.6 kcal/mol for HMX¹⁹. For PETN this

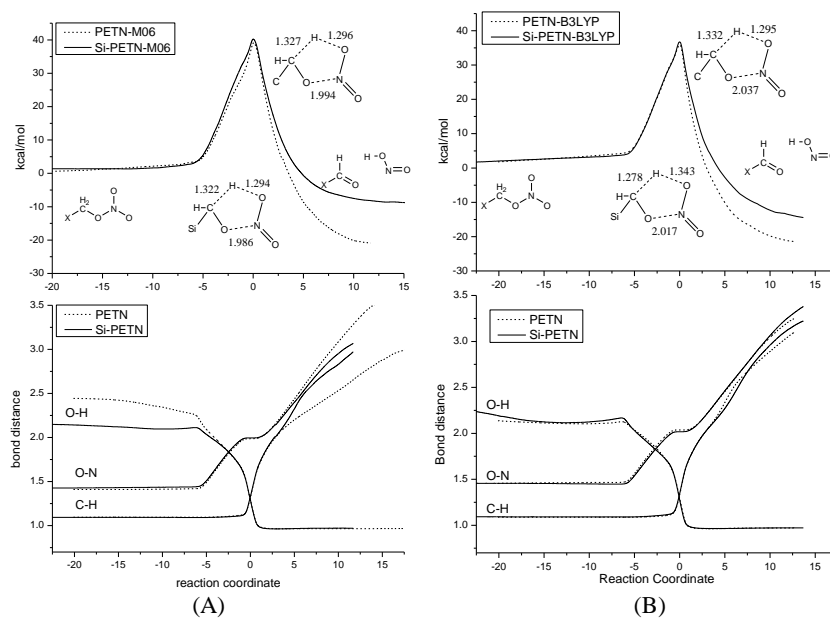


Figure 2-4 HONO dissociation pathway of PETN and SiPETN by (A) M06 (B) B3LYP

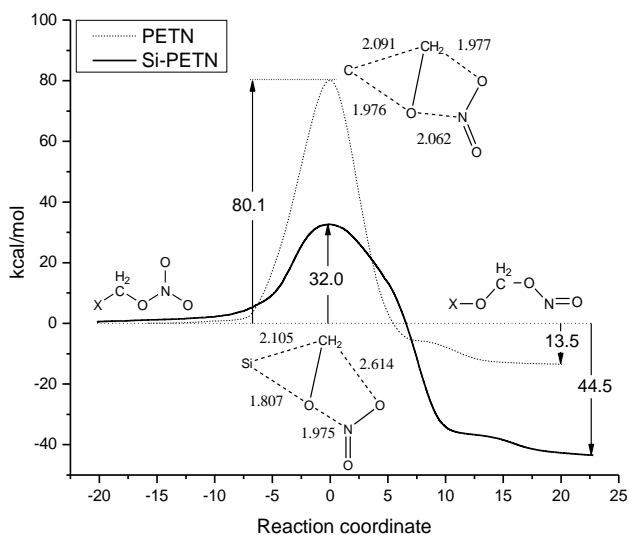


Figure 2-5. Energy vs. reaction coordinate and the geometry of the transition state (from DFT at the M06/6-311G** level). The IRC step is 0.1 a.u. with mass-weighted coordinate.

PETN is formed by bending the C-ONO₂ angle, breaking the partial Si-C bond, and making Si-O bond concurrently, as shown in Figure 2-5. This was studied by first locating the transition structure through 2-D scans followed by intrinsic reaction coordinate (IRC) scans. We find that Si-PETN has a 32.0 kcal/mol barrier for this rearrangement, which is dramatically *lower* than the value of 80.1 kcal/mol for PETN. This is partly due to the larger size of silicon (Si covalent radius of 1.17 Å compared to 0.771 Å for C²¹) resulting in a more stable five-coordinate transition state in Si-PETN, allowing the Si-C bond and Si-O bond to be shorter with the O-N bond broken later thereby decreasing the energy barrier significantly. Besides, Si is more electropositive than C, resulting in larger Si-O bond energy and therefore lower barrier for this rearrangement. Murray et al.²² applied reaction force analysis and found that most of the difference between the rearrangement barriers for PETN and Si-PETN is that Si-PETN benefits from a 1,3 electrostatic interaction involving a positive sigma-hole on the silicon and the negative linking oxygen, leading to the same conclusion.

An additional important factor in detonation sensitivity and a second dramatic difference between PETN and Si-PETN is the heat release which is 44.5 kcal/mol exothermic for reaction 5 with Si-

leads to TS energies of 39.2 (C) and 39.4 (Si), very similar to reaction 1. Such a tiny difference would not explain the huge difference in sensitivity.

Finally we considered the attack of the γ O on the α central C/Si atom, reaction 5, in which the β CH₂ group stays bonded to the γ O as the X-O bond forms simultaneously to a terminal O of the NO₂. Thus, the transition state in Si-

PETN, whereas the favorable decomposition for PETN (reaction 1) is 39.0 kcal/mol endothermic. To estimate the difference between two exothermic reactions in Si-PETN, the corresponding unimolecular decomposition rates of reaction 4 and 5 were calculated using the transition state theory²³. Assuming no tunneling, the rate of reaction 5 is 1.6×10^4 times faster than reaction 4 at 298K (see SI), making it plausible that reaction 5 may contribute significantly to sensitivity.

This mechanism also explains the Si-NMR spectroscopy of the decomposition product from Si-PETN, which contains the signal for siloxane $-\text{OSi}-(\text{CH}_2\text{OR}_2)\text{O}-$. Reaction 5 is similar to the Brook rearrangement²⁴ of the silyl group in silyl alcohols from carbon to oxygen, but this analog reaction cannot reach the transition state without breaking the O-H bond leading to a calculated barrier of 83.3 kcal/mol²⁵. In Si-PETN the α -silyl alcohol is replaced by the α -silyl nitro-ester and a flexible bond angle with a weak O-N bond, all of which favors the reaction 5 rearrangement product by dramatically decreasing the TS energy.

Conclusion

DFT calculations have identified a novel carbon-oxygen rearrangement of the newly synthesized Si derivative of the PETN energetic molecule that provides a plausible explanation of the dramatic increase in sensitivity observed experimentally. The results are concluded in Table 2-2. The

Table 2-2. The BDE of each bond and energies of transition state. All energies in kcal/mole.

Reaction	PETN		SiPETN	
	B3LYP ^a	M06 ^a	B3LYP ^a	M06 ^a
1: O-NO ₂ (BDE)	35.8	39.0	28.7	35.6
2: C-ONO ₂ (BDE)	73.3	82.2	69.4	77.6
3: C-X (TS)	41.7	49.1	40.6	48.2
4: HONO (TS)	36.2	39.2	36.5	39.4
5: O-X (TS)	73.1	80.1	30.5	32.0

^a Numbers listed here are DFT using the 6-311G** basis set .

^b The most recent experimental BDE is 39.5kcal/mol after correcting for the zero point energy correction and thermal correction to 298.15K indicating that the M06 results more accurate than B3LYP.

primary factors leading to this are the much stronger Si-O bond over C-O, the ability of the much larger Si to adopt the 5-coordinate transition state required for reaction 5, and the ability of the terminal O of NO₂ to stabilize this 5-coordinate transition state. In addition to the significantly lower barrier (32 vs. 80 kcal/mol), reaction 5 is also far more exothermic (45 vs. 13 kcal/mol) because a new Si-O bond is formed. This provides a large net energy release at very early stages of Si-PETN decomposition facilitating a fast temperature increase and expansion of the reaction zone. This combination of kinetic and thermodynamic enhancement factors for the Si analog illustrates a path to controlled sensitivity of other Si analogs of energetic molecules.

References

1. Klapotke, T. M.; Krumm, B.; Ilg, R.; Troegel, D.; Tacke, R., *J. Am. Chem. Soc.* **2007**, *129* (21), 6908-6915.
2. Dick, J. J.; Mulford, R. N.; Spencer, W. J.; Pettit, D. R.; Garcia, E.; Shaw, D. C., *J. Appl. Phys.* **1991**, *70* (7), 3572-3587.
3. Czerski, H.; Proud, W. G., *J. Appl. Phys.* **2007**, *102* (11), 8.
4. Field, J. E.; Bourne, N. K.; Palmer, S. J. P.; Walley, S. M.; Smallwood, J. M., *Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences* **1992**, *339* (1654), 269-283.
5. Tokmakoff, A.; Fayer, M. D.; Dlott, D. D., *J. Phys. Chem.* **1993**, *97* (9), 1901-1913.
6. Cai, Y.; Zhao, F. P.; An, Q.; Wu, H. A.; Goddard, W. A.; Luo, S. N., *J. Chem. Phys.* **2013**, *139* (16), 164704.
7. Zhu, W.; Xiao, H., *Struct. Chem.* **2010**, *21* (3), 657-665.
8. Murray, J. S.; Lane, P.; Politzer, P.; Bolduc, P. R., *Chem. Phys. Lett.* **1990**, *168* (2), 135-139.
9. Murray, J. S.; Lane, P.; Politzer, P., *Mol. Phys.* **1995**, *85* (1), 1-8.

10. Jaguar, v., Schrödinger, LLC, New York, NY, **2007**.
11. Lee, C. T.; Yang, W. T.; Parr, R. G., *Physical Review B* **1988**, *37* (2), 785-789.
12. Zhao, Y.; Truhlar, D. G., *Acc. Chem. Res.* **2008**, *41* (2), 157-167.
13. Shao, J. X.; Cheng, X. L.; Yang, X. D.; He, B., *Chinese Physics* **2006**, *15* (2), 329-333.
14. Luo, Y. R., *Handbook of Bond Dissociation Energies in Organic Compounds, New York: CRC Press* **2003**.
15. Volltrauer, H. N., *J. Hazard. Mater.* **1982**, *5* (4), 353-357.
16. Hiskey, M. A.; Brower, K. R.; Oxley, J. C., *J. Phys. Chem.* **1991**, *95* (10), 3955-3960.
17. Ng, W. L.; Field, J. E.; Hauser, H. M., *Journal of the Chemical Society-Perkin Transactions 2* **1976**, (6), 637-639.
18. Chakraborty, D.; Muller, R. P.; Dasgupta, S.; Goddard, W. A., *J. Phys. Chem. A* **2000**, *104* (11), 2261-2272.
19. Chakraborty, D.; Muller, R. P.; Dasgupta, S.; Goddard, W. A., *J. Phys. Chem. A* **2001**, *105* (8), 1302-1314.
20. Ng, W. L.; Field, J. E.; Hauser, H. M., *J. Appl. Phys.* **1986**, *59* (12), 3945-3952.
21. Pauling, L., *The Nature of the Chemical Bond, Cornell University Press* **1960**.
22. Murray, J. S.; Lane, P.; Nieder, A.; Klapotke, T. M.; Politzer, P., *Theor. Chem. Acc.* **2010**, *127* (4), 345-354.
23. de Bruin, T. J. M.; Lorant, F.; Toulhoat, H.; Goddard, W. A., *J. Phys. Chem. A* **2004**, *108* (46), 10302-10310.
24. Brook, A. G., *Acc. Chem. Res.* **1974**, *7* (3), 77-84.
25. Yu, Y. M.; Feng, S. Y., *J. Phys. Chem. A* **2004**, *108* (36), 7468-7472.